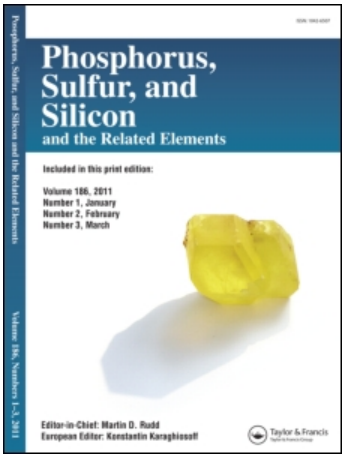

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Synthesis of Penta- and Hexa-*m*-Phenylenecyclophosphites and Thiophosphates

Eduard E. Nifantyev[a]; Elena N. Rasadkina[a]; Inna V. Yankovich[a]; Larisa K. Vasyanina[a]
[a] Chemical Faculty, Lenin Pedagogical State University, Moscow, Russia

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Short Communication

SYNTHESIS OF PENTA- AND HEXA-*m*-PHENYLENECYCLOPHOSPHITES AND THIOPHOSPHATES

EDUARD E. NIFANTYEV*, ELENA N. RASADKINA, INNA V. YANKOVICH and LARISA K. VASYANINA

Chemical Faculty, Lenin Pedagogical State University, per. Nesvizhskii 3, Moscow, 119021 Russia

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New representatives of an original crown ether class-penta- and hexaresorcinolamidophosphites (**7a,b** and **13a,b**)-were synthesized using the molecular assemblage technique. Their thio derivatives (**8a,b** and **14a,b**) were obtained, as well as the rhodium (I) complex of hexaphosphite **13b** (**16**). Macrocycle **15** containing both P^{3+} and P^{5+} was synthesized. ^1H and ^{31}P NMR spectroscopy data suggested the higher conformational flexibility of phosphite macrocycles.

Keywords: macroheterocyclic compounds; crown ethers; cyclophosphorylation; amidophosphites

INTRODUCTION

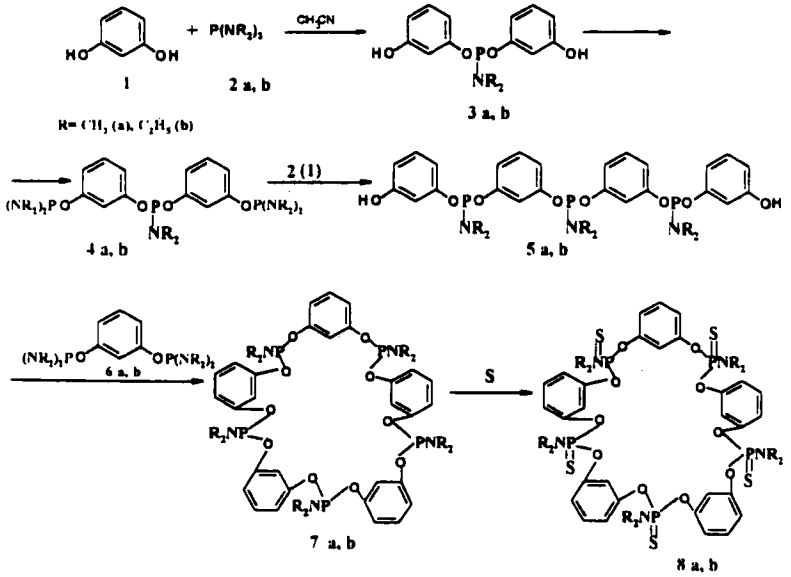
We recently obtained the first representatives of an original class of crown ethers with regularly alternating aromatic nuclei and phosphorus acid residues[1]. The compounds synthesized are relatively simple in composition: their cycles include only 2–4 phosphorus functional groups. These cyclic systems are of low diameters, which results in angular strain. Thus, phosphite and thiophosphate derivatives of the simplest crown ethers are

* Corresponding author

differing in conformation. In the context of the foregoing, we sought ourselves the task of synthesizing higher crown ethers with larger cavities.

RESULTS AND DICUSSION

In this paper we report the synthesis of penta- and hexaresorcinolamidophosphites using the molecular assemblage technique. Triamides of phosphorous acid and resorcinol were used as starting compounds:

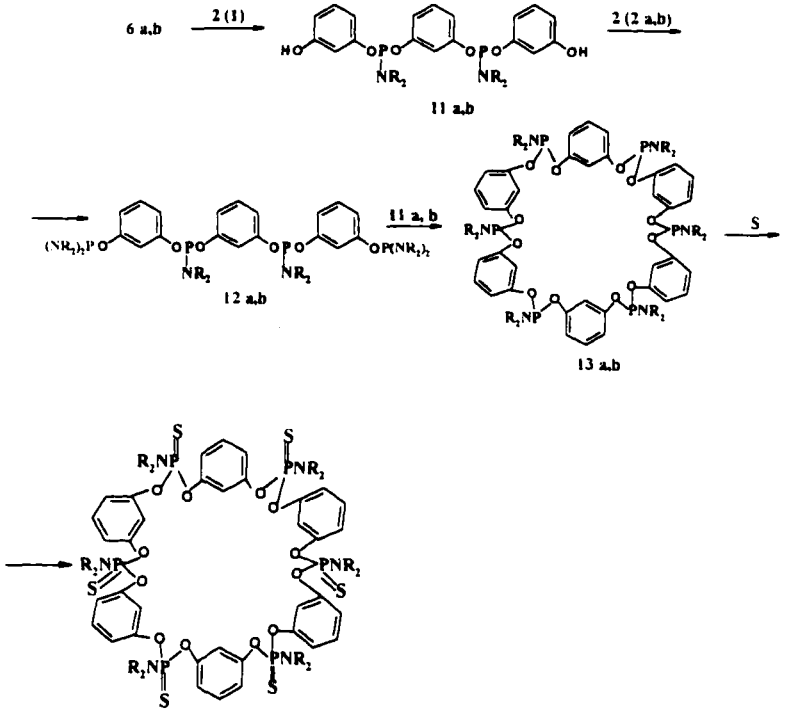


It should be noted that all reactions, including sulfurization, proceeded quickly at the room temperature. Compounds **4b** and **5b** were synthesized in this work and isolated as thio derivatives **9** and **10**.

Phosphacrown ethers **7a,b** were obtained as oils, whose ^{31}P NMR spectra shown singlets in the range characteristic of amidophosphites. They were transformed into thio derivatives (**8a,b**) for more thorough identification. After chromatographic purification, the thiophosphates differed in physicochemical and spectral characteristics. Compound **8a** was a solid; its ^{31}P NMR spectrum exhibited two singlets with different integral intensities, which was evidence of the nonequivalent nature of phosphorus

atoms in the molecule due to steric factors. The molecular mass of **8a** confirmed the presence of five main fragments in its molecule. Thiophosphate **8b** was isolated as viscous oil, whose ^{31}P NMR spectrum exhibited only singlet in the thiophosphate range.

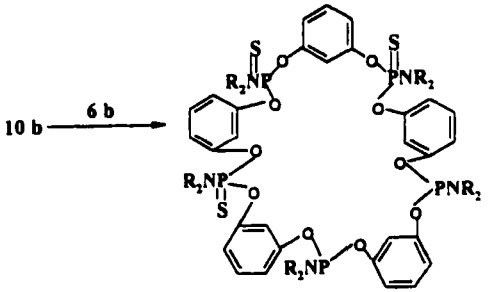
Macrocycles **13a,b** containing six resorcinol moieties were synthesized as follows:



Cyclic amidophosphites **13a,b** were isolated as viscous oils; their ^{31}P MNR spectra exhibited two singlets at 139.5 and 139.86 ppm (**13a**) and a singlet at 141.06 ppm (**13b**). The cyclophosphites obtained, were transformed without additional purification, into thio derivatives **14a,b**. It is noteworthy that the ^{31}P NMR spectra of both thiophosphates exhibited four singlets in the characteristic range of thiophosphates containing aromatic substituents and that their ^{1}H NMR spectra showed broadened signals for all proton groups. We believe that these changes in spectral characteristics, observed on going from the P^{3+} macrocycles to their P^{5+}

derivatives, are associated with the decrease in the degree of freedom for the phosphorus atoms and the formation of conformations with maximally nonequivalent phosphorus and hydrogen atoms. The presence of different substituents at the nitrogen atom also affects the conformational flexibility of the molecule, which increases on going from N-Me_2 to N-Et_2.

In addition, we accomplished the synthesis of macrocycle **15** containing both trivalent and pentavalent phosphorus atoms:



15

Two singlets at 140.5 and 66.1 ppm with the integral intensity ratio of 2 : 3 were observed in the ^{31}P NMR spectrum of **15**. We believed that the migration of sulfur atoms between all phosphorus atoms was possible in the molecule of regular structure. However, no variations were observed in the ^{31}P NMR spectrum between 34 and 110°C. This confirmed the assumed irregular structure of these molecules.

The rhodium complex **16** with the ligand-to-metal ratio of 1 : 6 was also obtained from macrocycle **13b** and Rh[(*acac*)$(CO)_2$].

EXPERIMENTAL

^1H NMR spectra of compounds **8b, 14a, 14b, 9, 10**, and **15** in C_6D_6 were recorded on a Bruker WH-250 instrument at 250 MHz; those of **8a** and **16** in C_6D_6were recorded on a Bruker AC-200 instrument at 200 MHz with TMS as an internal standard. ^{31}P NMR spectra of **7a, 7b, 13a**, and **13b** in acetonitrile and those of **8a, 8b, 9, 10, 14a, 14b, 15**, and **16** in benzene were recorded on a Bruker WP-80 SY at 32.4 MHz (85% H_3PO_4 being used as an external standard).

Column chromatography was carried out on L 100/250 silica gel; TLC was conducted on Silufol plates using (A) benzene: (B) benzene-dioxane 3 : 1, (C) 5 : 1, and (D) 10 : 1; (E) hexane-dioxane 3 : 1; and (F) chloroform-ethanol 5 : 1 as eluants. The detection of compounds was achieved using iodine vapor treatment, calcination, and the treatment with a 1% aqueous solution of $AgNO_3$.

We have synthesized amidophosphites **3a,b**[2] and bis(tetraalkyldiamidophosphitoxybenzenes) **6a,b**[1] previously.

Cyclopenta(m-phenylenedialkylamidothionophosphates) (8a,b)

Hexaalkyltriamide of phosphorous acid **2a** or **2b** (1.7 mmol) was added to a solution of 3.4 mmol of resorcinol (**1**) in 17 ml of acetonitrile, and the reaction mixture was stirred at room temperature for 1.5 h. Then, 3.4 mmol of **2a** or **2b** was added, and the mixture was stirred for 2 h. More 3.4 mmol of **1** in 17 ml of acetonitrile was added; the mixture was stirred for 2 h, and 1.7 mmol of 1,3-bis(tetraalkyldiamidophosphitoxybenzene) **6a,b** was added. The reaction mixture was left to stand overnight. Acetonitrile was removed the reaction products (**7 a,b**) were dissolved in 15 ml of benzene; 4.25 mmol of dry sulfur was added to the solution, and the mixture was stirred at room temperature for 3 h. The solvent was evaporated, and the residue was chromatographed on a column; compounds **8a,b** were eluted by system F and dried for 3 h *in vacuo* (mm Hg, 50°C).

Cyclopenta(m-phenylenedimethylamidothionophosphate) (8a)

Yield, 2.97 g (65%); m.p 189°C, R_f 0.72 (E). ^{31}P NMR: δ 66.93 s, 67.64 s. ^1H NMR: δ 2.66 (b m, CH_3, 30H), 7.10 b m, 7.18 b m, 7.55 b s, 7.62 b s, 7.69 b S (CH-ar, 20H). Anal. Calcd for $C_{40}H_{50}N_5O_{10}P_5S_5$; P 14.39. M 1076. Found: P 14.55. M 1045 (cryosc.).

Cyclopenta(m-phenylenediethylamidothionophosphate) (8b)

Yield, 3.2 g (63%); viscous oil; R_f 0.64 (E), 0.43 (F). ^{31}P NMR: δ 66.29. ^1H NMR: δ 0.94 (b m, CH_3, 30H), 3 24 (b m, CH_2, $^3J_{P\text{-}H}$ 13.66 Hz, 20H), 6.93 b m, 7.08 b m, 7.54 b S (CH-ar, 20H). Anal. Calcd for $C_{50}H_{70}N_5O_{10}P_5S_5$; P 12.73. Found: P 12.85.

Bis(m-tetraethyldiamidothiophosphatoxyphenyl) diethylamidothionophosphate (9)

Compound **2b** (0.37 g, 1.49 mmol) was added to 2.97 mmol (0.33 g) of **1** in acetonitrile; the mixture was stirred for 1.5 h. More 2.97 mmol (0.74 g) of **2b** was added, and the mixture was left to stand for 2 h. Then, 4.47 mmol (0.143 g) of sulfur was added to the solution obtained, and the reaction mixture was stirred for 4 h. The solvent was removed *in vacuo*; the residue was chromatographed on a column, eluting the product **9** with system C. Yield, 0.775 g (68%); viscous oil; R_f 0.72 (F). ^{31}P NMR: δ 66.17 s, 75.90 s. ^1H NMR: δ 0.95 (t, CH_3, 30H), 3.11 (b m, CH_2, 20H), 6.47 (b s, OH, 2H), 7.04 b m, 7.48 b d (CH-ar, 8H). Anal. Calcd for $C_{32}H_{58}N_5O_4P_3S_3$ P 12.13. Found: P 12.08.

Bis[(m,m′-hydroxyphenyl-diethylamidothiophosphatoxy)phenyl]-diethylamidothionophosphate (10)

Compound **4b** (1.45 g, 2 mmol) was added to a solution of 4 mmol (0.44 g) of **1** in 20 ml of acetonitrile; the mixture was stirred for 1.5 h. More 6 mmol (0.19 g) of sulfur was added, and the mixture was stirred at room temperature. The solvent was removed; the residue was chromatographed on a column, eluting the product **10** with system D. Yield, 1.2 g (72%); viscous oil; R_f 0.36 (F). ^{31}P NMR: δ 66.27 s, 66.22 S. ^1H NMR: δ 0.93 (t, CH_3, 18H). 3.25 (m, CH_2, $^3J_{P\text{-}H}$ 12.66 Hz, 12H), 6:47 (b s, OH, 2H), 6.87 b m, 6.96 b m, 7.52 b s (CH-ar, 16H). Anal. Calcd for $C_{36}H_{48}N_3O_8P_3S_3$; P 11.06. Found: P 11.10

Cyclohexa(m-phenylenedialkylamidothionophosphates) (14a,b)

Compound **2a** or **2b** (1.73 mmol) was added to 3.46 mmol of **1** in 17 ml of acetonitrile; the mixture was stirred at room temperature for 2 h. Then the solution obtained was divided into two equal parts. More 1.73 mmol of **2a** (or **2b**) was added to the first part. The mixture was stirred for 2 h; the second part of the solution obtained was added, and the reaction mixture was left to stand overnight. Acetonitrile was removed; the residue (**13 a, b**) was dissolved in 15 ml of benzene. Dry sulfur (5.2 mmol) was added, and the mixture was stirred for 3 h. The solvent was removed *in vacuo*; the residue

was chromatographed on a column, eluting the products with systems A (**14a**) and B (**14b**).

Cyclohexa(m-phenylenedimethylamidothionophosphate) (14a)

Yield, 4.83 g (72%); p.m. 167°C; R_f 0.71 (B). ^{31}P NMR: δ 66.21 s, 67.22 s, 66.54 s, 67.16 s. ^1H NMR: δ 2.61 (m, CH_3, 36H), 6.93, 7.02, 7.52, 7.58 (b m, CH-ar, 24H) Anal calcd for $C_{48}H_{60}N_6O_{12}P_6S_6P$ 14.39. M 1291. Found: P 14.50, M 1263 (cryosc.)

Cyclohexa(m-phenylenediethylamidothionophosphate) (14b)

Yield, 5.08 g (67%); viscous oil; R_f 0.65 (F). ^{31}P NMR: δ 65.12 S, 65.67 S, 66.21 S, 66.93 S ^1H NMR: δ 0.95 (m, CH_3, $^2J_{H-H}$ 6.83 Hz, 36H), 3.24 (m, CH_2, $^3J_{P-H}$ 12.81 Hz, 24H), 7.03 m, 7.13 b d, 7.59 b S (CH, 24H). Anal. calcd for $C_{60}H_{84}N_6O_{12}P_6S_6$ P 12.73. Found: P 12.68.

Cyclo[bis(m-phenylenediethylamidophosphite)-tris (m-phenylenediethylamidothionophosphate)] (15)

Bisphosphite **6b** (1.04 g, 3.0 mmol) was added to a solution of 3.0 mmol (2.5 g) of **10** in 10 ml of acetonitrile: the mixture was stirred for 48 h. The solvent was removed *in vacuo* to minimum, and hexane was added. The oil formed was separated and dried *in vacuo* for 3 h (1 mm Hg, 55–60°C). Yield, 2.21 g (56%); viscous oil; R_f0.47 (C). ^{31}P NMR: δ 140.56 s, 66.11 s. ^1H NMR: δ 0.97 (t, CH_3, 30H), 3.37 (b, CH_2, 20H), 7.01, 7.12, 7.6 (b m, CH-ar. 20H). Anal. Calcd for $C_{50}H_{70}N_5O_{10}P_5S_3$; P 13.44. Found: P 13.56.

μ-[Cyclohexa(m-phenylenediethylamidohexaphosphite)]hexa (acetylacetonatocarbonylrhodium(I)) (16)

Rh[(*acac*)$(CO)_2$] (0.052 g, 0.019 mmol) was added to a solution of 0.033 mmol (0.043 g) **7b** in 5 ml of benzene. The mixture was held at room temperature for 2 h. The solvent was evaporated; the residue was washed with hexane and redissolved in benzene, and 3 ml of hexane was added. The precipitate formed was separated and dried *in vacuo* for 2.5 h

(1 mm Hg, 45°C). Yield, 0.077 g (85%); light yellow powder, decomp. p. 110°C; R_f 0 (C), 0.85 (G). ^{31}P NMR: δ 133.86 d ($^{1}J_{Rh-H}$ 263.10 Hz). ^{1}H NMR: δ 1.10 (b t, CH_3, 30H), 1.72 (b s, CH_3-*acac*, 18H), 1.93 (b s, CH_3-*acac*, 18H), 3.62 (b m, CH_2, 20H), 5.34 (s, CH-*acac*, 12H), 7.09, 7.45, 7.70 (b m, CH-ar, 20H). IR spectrum: ν 1990 (CO-Rh), 1510, 1570 (*acac*). Anal. Calcd for $C_{96}H_{126}N_6O_{30}P_6Rh_6$ P 7.42. Found: P 7.53.

Acknowledgements

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